Advanced Engineering Letters **Vol.2, No.3, 81-87 (2023)** **e-ISSN: 2812-9709**

PREPARATION AND CHARACTERIZATION OF EGGSHELLS POWDERS TREATED WITH HYDROCHLORIC ACID AND SODIUM HYDROXIDE

UDC:637.412:620.11
Original scientific paper https://doi.org/adeletters.2023.2.3.1

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Abstract:
The present paper investigates the possibility of increasing the porous and surface characteristics of eggshell powders. For this purpose, the collected waste eggshells were washed, dried at 90°C, crushed mechanically and sieved into a particle size smaller than 0.315 μm. The resulting powder was chemically modified by immersion in 1M solutions of HCl and NaOH. After the treatment with the above reagents, the surface-treated eggshells were characterized by a combination of XRD, FT-IR, BET and SEM analyses. The XRD diffraction data and FT-IR spectra confirmed that the untreated eggshells were composed mainly of calcium carbonate in the form of calcite. After treatments on the surface of the particles were carried out, calcite did not undergo structural changes. From the N_2 adsorption-desorption isotherms it was found that all of samples have nonporous or macro porous structures.

ARTICLE HISTORY
Received: 2 April 2023
Revised: 7 July 2023
Accepted: 26 July 2023
Published: 30 September 2023

KEYWORDS
Waste eggshells, calcium carbonate, treatment, surface characteristics, pore volume, specific surface area, structure

1. INTRODUCTION

Calcium carbonate occurs in nature in the form of minerals in metamorphic marble and sedimentary rocks [1]. In addition to natural minerals, there are a number of industrial waste materials with a high content of calcium carbonate, e.g. chicken eggshells, various sea shells etc.

Every year the consumption of eggs from various sources increases, leading to the generation of significant amounts of eggshell waste. Most of the eggshell waste is accumulated without pre-treatment [2]. Instead of being dumped in landfills, efforts have been made recently to convert eggshell waste into products with several applications [3-5].

Numerous scientific publications in the literature of various research groups are dedicated to eggshell waste, which shows their potential for application in materials science [6–11]. These main applications include the use of eggshell waste as a food additive [8], for organic synthesis [7], in catalysis [12, 13], adsorption [14, 15], as a possible bone substitute [16], starting material for the preparation of bioceramics [16], as a filler for composite materials [17-19] or reinforced biopolymer composites and others. In recent years, considerable interest has been in materials synthesis using waste eggshells in green tribology [20, 21].

Despite the potential of eggshells as an alternative to calcium carbonate, after proper treatment of their waste, the scope of their application can be further expanded. Determination of properties such as surface area and porosity of eggshell powder is crucial in developing value-added products. Surface roughness is another important parameter affecting the surfaces' tribological behavior and can be measured by various techniques [22].

Two main groups of treatment methods for eggshells can be distinguished. The first group includes methods for treating eggshells at high temperatures. In them, the calcium carbonate included in the composition of the shells is transformed into CaO. The second group of methods includes those in which the eggshells are

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not subjected to high-temperature treatment and the calcium carbonate does not undergo structural changes. One of the possibilities for realizing this is to treat the eggshell particles with various chemical reagents such as bases [19, 23-26], HNO_3 acid [27], stearic acid [28-30], etc.

The present paper aims to determine the effect of direct chemical treatment with hydrochloric acid and sodium hydroxide on the surface and porous characteristics of waste eggshell powders. In order to evaluate the changes in the characteristics mentioned above, the prepared, treated samples were characterized, and the results obtained were analyzed and compared with those of the untreated ones and commercial calcium carbonate.

2. MATERIALS AND METHODS

2.1 Materials

1M standard solutions of hydrochloric acid (HCl) and sodium hydroxide (NaOH), products of Sigma-Aldrich, were used as reagents for surface treatment of waste eggshells. Commercial calcium carbonate with chemical formula ($CaCO_3$), molecular weight 100.09 g/mol and purity 99%, product of Sigma-Aldrich, was used to compare the surface characteristics of waste eggshells before and after chemical treatment.

2.2 Preparation of waste eggshells

The collected waste eggshells were washed with hot tap water without removing the membrane and left in the air for 24 hours. Then they were dried in an air oven at 90°C to constant weight. The dried eggshells were crushed mechanically and sieved. The selected fraction with a particle size smaller than 0.315 µm was stored in containers for further characterization and chemical treatment.

2.3 Eggshells chemical surface treatment

After immersion in the modifying solutions, the eggshell powder was chemically modified by the direct method: 50 g of eggshell powder was soaked in 1M solution of HCl or NaOH under stirring at room temperature for 24 hours at 420 rpm. After the treatment with the above reagents, the resulting modified eggshells were filtered, dried and stored in glass containers at room temperature until their characterization. Eggshell samples treated with HCl and NaOH were designated as HCl-ES and NaOH-ES, respectively.

2.4 Characterization

To identify the changes caused by the different treatments of eggshells powder surface, SEM analysis was carried out on a JSM 6390 electron microscope (Japan). To estimate the effect of modifying agents on the chemical structures, the samples were analyzed by X-ray diffraction analysis (XRD) using a PANalytical Empyrean apparatus and Fourier Transform Infrared Spectroscopy (FT–IR) on a spectrophotometer Nicolet iS 50 FT-IR Thermo Scientific. The porous characteristics of the eggshell samples were obtained through BET analysis on an apparatus Surfer sorption analyzer (Thermo Scientific) using N_2 adsorption-desorption isotherms at –196°C. The results obtained were compared to those from commercial calcium carbonate $CaCO_3$.

3. RESULTS AND DISCUSSION

In order to obtain information on the chemical composition and to identify the crystalline phases present and the changes caused by the different treatments of eggshell powders, XRD analysis was carried out. Table 1 shows the XRD diffraction peaks observed and their relative intensity for waste eggshells before and after chemical treatment with NaOH and HCl. The diffraction peaks observed do not change due to surface treatment and their number is the same as that of $CaCO_3$ – Table 2.

Table 1. Diffraction peaks observed in the XRD patterns of waste eggshells before and after chemical treatment

Diffraction peaks registered 2ϑ, degree	Relative intensity, %		
	ES	HCl-ES	NaOH-ES
29.42	100	100	100
35.99	6.03	6.03	18.06
39.42	13.09	7.03	10.89
43.17	9.20	4.30	10.82
47.53	12.87	7.08	7.77
48.50	12.79	8.47	11.37
57.39	4.56	2.44	5.47
61.40	1.78	1.26	1.88

It shows the data for the registered diffraction peaks, d-spacing, the Miller indices and the relative intensity of the peaks at diffraction angles (2ϑ) of the commercial $CaCO_3$ used. Comparing the obtained data with those in the reference databases, it was confirmed that the XRD diffraction data from Table 2, correspond to those reported in the literature for the crystalline phase of calcite [31]. This proves that no new phases were formed in the untreated and treated eggshells, i.e. they are made entirely of calcite.

Table 2. XRD diffraction data for commercial $CaCO_3$

Diffraction peaks registered 2ϑ, degree	hkl	d-spacing, Å	Relative intensity, %
29.42	104	3.0353	100
35.99	110	2.4951	11.74
39.42	113	2.2856	16.43
43.17	202	2.0954	14.36
47.53	018	1.9130	19.80
48.50	116	1.8765	17.83
57.39	122	1.6054	7.61
61.40	119	1.5100	2.07

The XRD diffraction patterns in the interval 2ϑ = 5 – 80° of treated Na-ES and HCl-ES are quite similar to the raw eggshells (Fig. 1), except for their intensity, which can be attributed to the presence of a protein membrane from the eggshell.

Modification of eggshells by chemical treatment results in the removal of the organic part of the shell. The acid treatment with 1 M HCl resulted in the organics' release and was insufficient to interact the acid with the calcite from the shell. Therefore, the acid-treated HCl-ES shells' intensity and crystallinity were the highest.

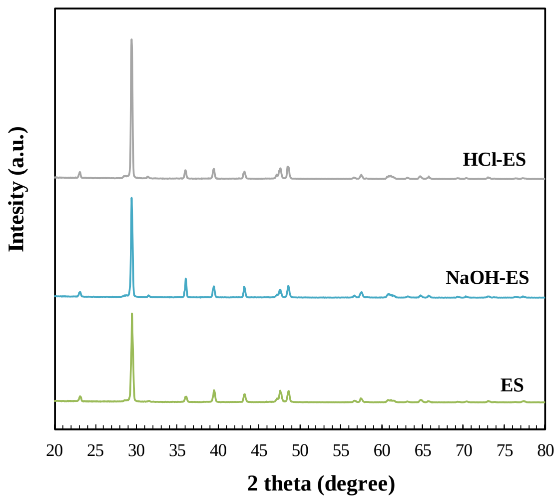

Fig. 1. XRD diffraction patterns of waste eggshells before and after chemical treatment

Table 3 summarize characteristic peaks observed in the FT-IR spectra of commercial calcium carbonate used in this work. Fig. 2 presents changes observed in the spectra of the studied waste ES powders before and after surface treatment, registered in the region 4000–400 cm^{-1}. As can be seen from the figure, all the spectra are identical. They include the characteristic bands observed for $CaCO_3$ particles at 1420, 875, 712 cm^{-1} [32], 2874, 2982, and broadband at around 3420 cm^{-1} [33]. This suggests that untreated and treated eggshells are composed mainly of calcium carbonate in the form of calcite. It means that calcite did not undergo structural change after the treatment of the ES surface was carried out. FT-IR results are in good agreement with XRD data.

Table 3. Characteristic peaks observed in the FT–IR spectra of commercial $CaCO_3$

Wave length of the peaks registered, cm^{-1}	Assignment
712	in-plane bending vibrations of $-CO_3^{2-}$
875	out-of-plane bending vibrations of $-CO_3^{2-}$
1420	asymmetric stretching vibrations of $-CO_3^{2-}$
2874	symmetric stretching vibration of $-CH_2$, $-CH_3$
2982	asymmetric stretching vibration of $-CH_2$, $-CH_3$
3420	stretching vibrations of –OH groups

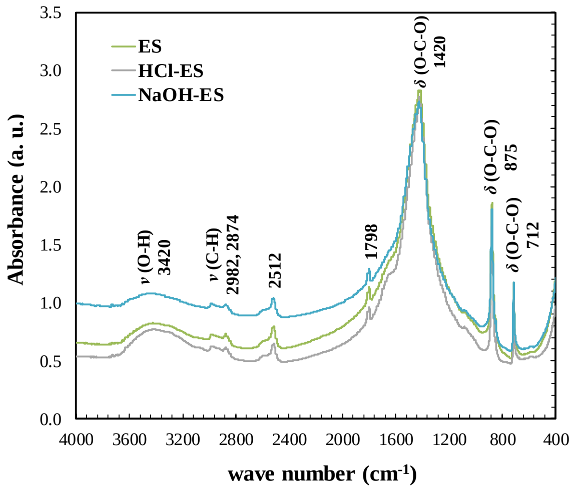

Fig. 2. FT–IR spectra of waste eggshells before and after chemical treatment

Table 4 shows the textural porous parameters of eggshells before and after chemical treatment with 1M HCl or NaOH. It was found that the determined Brunauer-Emmett-Teller surface area for untreated eggshells is 3.6654 m^2/g and pore volume 0.0064 cm^3/g. The results obtained are in accordance with those reported in the literature for pore volume from 0.00022 to 0.0065 cm^3/g [34]. The indicated characteristics are significantly improved after the ES surface treatment. For example, the alkaline treatment leads to higher values of the specific surface area of 4.2117 m^2/g and total pore volume of 0.0095 cm^3/g. The use of HCl increases the specific surface area by almost two times – up to 6.3244 m^2/g. The increase in surface area is probably a consequence of the formed pores in the structure of the eggshells, as was determined by SEM analysis – Fig. 3.

Table 4. Textural porous parameters of commercial $CaCO_3$, untreated and treated eggshells

Parameters	Commercial $CaCO_3$	Eggshell samples		
		ES	HCl-ES	NaOH-ES
BET surface area, m^2/g	3.4978	3.6654	6.3244	4.2117
Total pore volume, cm^3/g	0.0046	0.0064	0.0113	0.0095

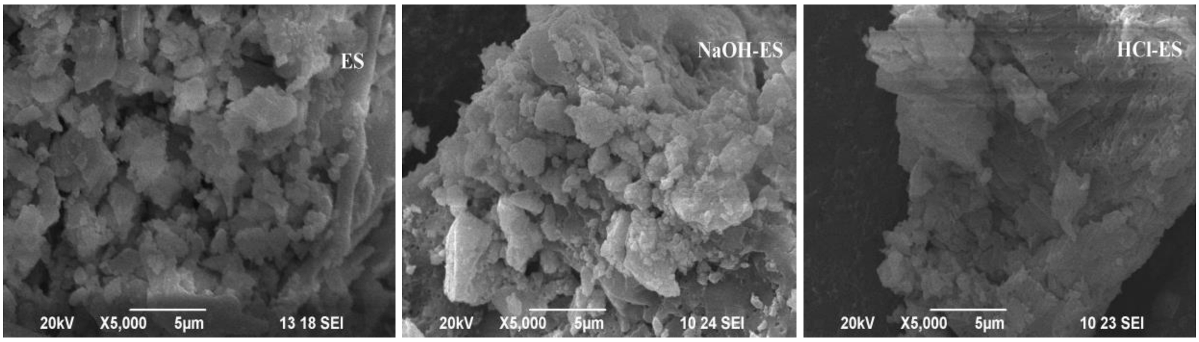

Fig. 3. SEM images of waste eggshells before and after chemical treatment

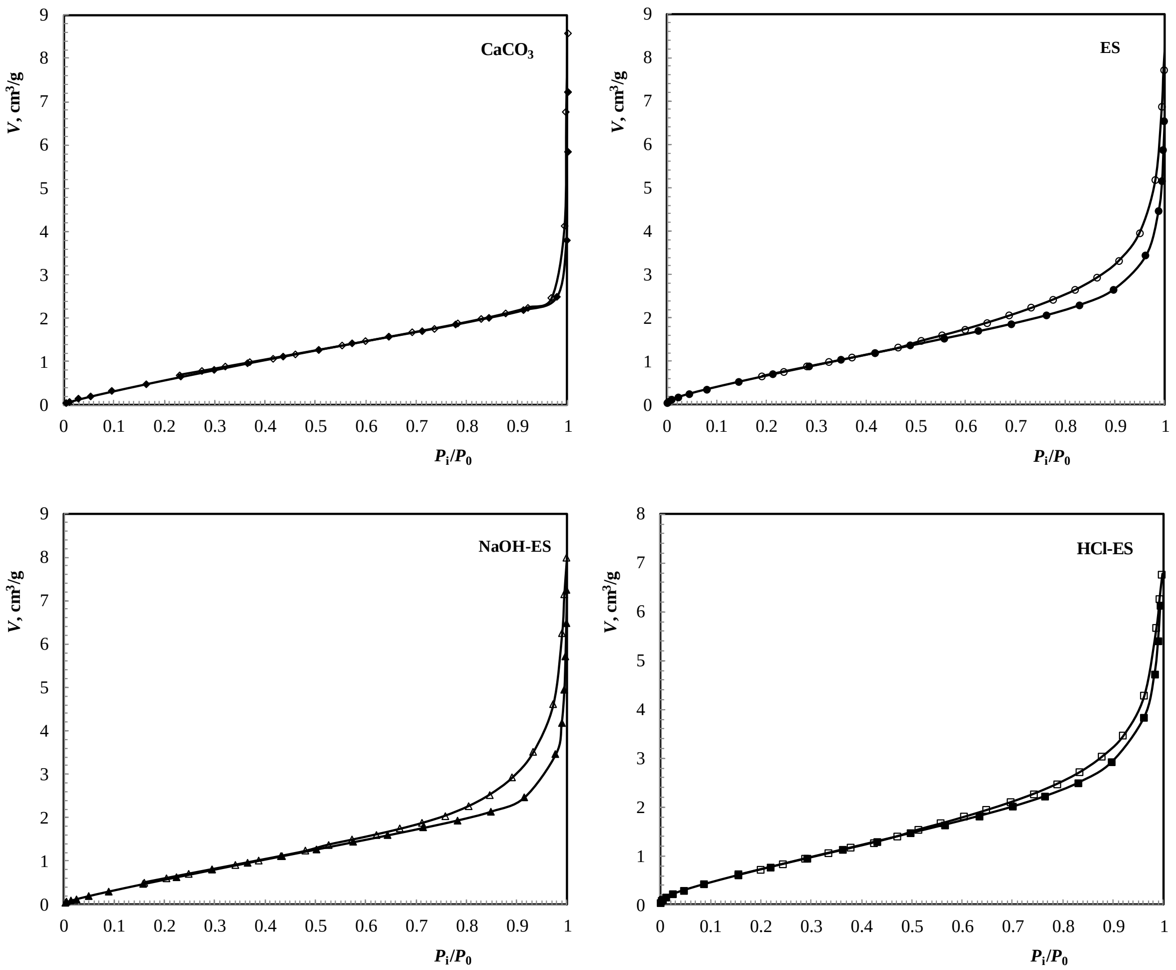

Fig. 4. N_2 adsorption-desorption isotherms of commercial $CaCO_3$, ES, HCl-ES and NaOH-ES powders

The nitrogen adsorption-desorption isotherms at –196°C of commercial $CaCO_3$, untreated and treated eggshells are shown in Fig. 4. The isotherms of all samples are of type II according to the IUPAC classification having H_3 type hysteresis loop, an indication that the products have nonporous or macro porous structures. Regardless of the surface treatments with various reagents, the latter does not affect the structure of eggshell powders.

The results showed that the modifying agent is crucial to the modification process. To improve the porous characteristics of the treated powders, it is necessary to use other modifying agents or carry out additional treatment of ES powders.

4. CONCLUSION

Surface-treated waste eggshells powders with hydrochloric acid and sodium hydroxide were prepared. The determined characteristics from SEM, XRD, FT-IR and BET analyses were compared to these of untreated eggshells and commercial calcium carbonate. From the observations in the XRD diffraction patterns and FTIR spectra, it was found that the chemical structure of waste eggshells, regardless of whether they were treated or not, was associated with carbonate minerals present in their composition. HCl treated eggshell samples showed a higher surface area (6.3244 m^2/g) than that for NaOH treated samples – 4.2117 m^2/g. The increase in surface area is a result of the pores formed in the structure of the eggshells as was determined from the morphological observations. However, the surface area and total pore volume values were low. To improve the porous characteristics of the treated powders in the future, it is necessary to use other modifying agents or carry out additional treatment on the surface.

ACKNOWLEDGMENTS

This work was supported by the Scientific Research Center at Assen Zlatarov University under the contract № 465/2022.

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